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THE PREDICTION OF THE
BURNING RATE EXPONENT OF SOLID PROPELLANTS

By

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December 1966

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SUMMARY

It has been postulated by the author that the burning rate exponent for solid propellant combustion can be represented by

$$n = \log (1/\text{Lewis number})$$

The Lewis number, Le, is a dimensionless ratio of mass diffusivity to thermal diffusivity. The Lewis number correlation is used in the paper to explain burning rate versus pressure behavior for various progressive, plateau, and regressive propellants. Qualitative prediction by the correlation of observed relationships of heat and mass transport, density, specific heat, and thermal conductivity is described. Discussion is also presented on use of the model to predict a critical density effect in deflagration-to-detonation phenomena.

Using a selected PBAA-ammonium perchlorate propellant as a base, the burning rate exponents of two other similar propellants were calculated. Calculated exponent values, using the Lewis number correlation, were within 10 to 25 percent of measured exponents.

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THE PREDICTION OF THE BURNING

RATE EXPONENT OF SOLID PROPELLANTS

BY

ROBERT J. HEASTON

INTRODUCTION

The combustion of solid propellants involves a complex coupling of transport phenomena and chemical kinetics. This paper attempts to identify and separate the effects caused by each of these mechanisms. The same model is also used to predict the characteristics and values of the burning rate exponent. A unique approach to this analysis is offered by the following equation:

$$r = b\,p^{\log(1/Le)} \tag{1}$$

where: r = regression rate

b = pre-exponential function

p = pressure

Le = Lewis number

$$= \frac{\rho D c_p}{k}$$

ρ = density

D = mass diffusivity

c_p = specific heat at constant pressure

k = thermal conductivity

The author first proposed equation 1 in correspondence to Green(1) and Ordahl(2). Some preliminary conclusions concerning equation 1 were published in a review paper by the author(3). Further analysis of equation 1 indicates that it is an interesting framework for separating the variables observed in solid propellant combustion.

This paper is divided into sections. Each section will begin with some prediction that may be made with equation 1. Immediately following each prediction made by equation 1 will be a discussion of related data from the literature. A transition will then be made

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to the next section. Over-all conclusions of the model, predictions, and available proof are given at the end of the paper.

MATHEMATICAL CURVES

Independent of any relationship to solid propellant combustion, equation 1 is a mathematical formula that can be graphed when appropriate numerical values are inserted for the variables. In logarithmic form equation 1 is as follows:

$$\log r = \log b + (\log 1/Le)\log p \qquad (2)$$

In a plot of log r versus log p, the value of log 1/Le will control the slope or curvature of the resultant curves. Thus, for arbitrary values of r, p, and b, figure 1 shows the curves for various Lewis numbers.

For Lewis numbers approaching zero, the value of r in figure 1 is increasing infinitely with increasing p. This condition is dependent upon the fact that the Lewis number is changing with p (or r for the purely mathematical case).

The widely known form of equation 1 is the de Saint Robert equation(4),

$$r = b\,p^n \qquad (3)$$

Equation 3 is an empirical formula where the exponent n is determined from experimental measurements on actual propellants. Different propellant formulations give different regression rate versus pressure relationships. Most propellants yield the characteristics(4) shown in figure 2.

In this case n is usually greater than zero but less than one. A constant slope is also maintained over a wide pressure range (a few pounds per square inch to several hundred pounds per square inch).

Some nitrocellulose propellants with small amounts of lead additives produce the curve(4) shown in figure 3. As a result of its characteristic shape, the formulation producing the curve in figure 3 is called a "plateau" propellant. A few ammonium perchlorate composite propellants also exhibit this behavior.

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Another unique relationship of regression rate and pressure is exhibited by so-called "mesa" propellants(4). This figurative name should be obvious from figure 4. A negative effect of the exponent n exists over a narrow pressure range.

In figures 2, 3, and 4, the values of n, from equation 3, are preferably less than one. The usual magnitudes, except for negative values, are 0.4 to 0.9. A low level is desirable. When n approaches or exceeds one, there is a definite danger of deflagration-to-detonation (DTD). In DTD, propellant regression increases almost infinitely fast with pressure until a steady state detonation is reached. Under these circumstances the exponent n is probably some function of pressure.

It is readily apparent that comparison of equations 1 and 3 yields the following:

$$n = \log (1/Le) \tag{4}$$

On a strictly numerical basis, all of the slopes depicted in figures 2 through 4 also are shown in figure 1. This relationship is the subject of the next section of this paper.

A HYPOTHETICAL PROPELLANT

A hypothetical composite of figures 1 through 4 is shown in figure 5. Four different zones are shown in figure 5. Zone 1 represents the normal propellant shown previously in figure 2. Using observed values of n of 0.1-0.7, the Lewis number can be calculated from equation 4. The resultant values are Le = 0.8-0.2. In zone 2 of figure 5, Le = 1.0 for n = 0. Similar determinations may be made for zones 3 and 4. Thus, all the values of the Lewis number presented in figure 1 also occur in figure 5. Every magnitude of n reported in figures 2-4 is repeated in figure 5. With the exception of zone 4, figure 5 is very much like figure 4. Instead of changing to a normal propellant slope in zone 4 in figure 5, a deflagration-to-detonation characteristic is substituted. The mesa of zone 2 is also more idealistic with a horizontal behavior. It is quite possible, then, that figure 5 is not so hypothetical after all.

REALISTIC LEWIS NUMBERS

The values of the Lewis numbers shown in figures 1 and 5 must have some physical significance or else the hypotheses made so far would be meaningless. The Lewis number is a dimensionless ratio that is often interpreted as the Prandtl number divided by the Schmidt number,

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$$Pr = \frac{C_p \mu}{k}, \quad \text{Prandtl number} \tag{5}$$

$$Sc = \frac{\mu}{\rho D}, \quad \text{Schmidt number} \tag{6}$$

In these dimensionless numbers the terms are the same as defined previously, except for μ which is viscosity. Dividing (5) by (6),

$$Le = \frac{Pr}{Sc} \tag{7}$$

Using values of Pr and Sc in Foust **et al**(5), the values of Le shown in table 1 are matched with a description of real gases. Real gases generally have Lewis numbers nearly equal to unity or slightly less. The Lewis numbers of liquids or gases at very high pressures are usually quite low. For the ideal case using a simple model gas, the transport diffusivities are equal (5). Since, alpha, the thermal diffusivity is

$$\alpha = \frac{k}{\rho C_p} \tag{8}$$

This means then, that

$$Le = \frac{D}{\alpha} \tag{9}$$

$$= \frac{\text{Mass diffusivity}}{\text{Thermal diffusivity}}$$

As stated above, the mass diffusivity and the thermal diffusivity are equal for simple, ideal gases. Consequently, Le = 1 for an ideal gas.

Unfortunately Lewis numbers are difficult to measure in real gas systems. It becomes even more difficult, if not impossible, to define Lewis numbers for a complex system, especially a burning solid propellant.

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CROSS-SECTIONS OF BURNING SOLID PROPELLANTS

In order to be a useful tool, the Lewis number must be defined for some part of the combustion zone that exists in burning solid propellants. The problem is even more difficult because there is some variation in the view-points of what actually occurs as a propellant burns. Solid propellants are usually a heterogeneous mixture of fuel, binder, and oxidizer. In an organic composite propellant, these ingredients are usually powdered aluminum, polymer, and ammonium perchlorate, respectively. A double-base propellant might contain powdered aluminum in a plasticized nitrocellulose formulation. Various additives are used to obtain different rate-pressure relationships. Under certain conditions one might also argue whether the oxidizer regresses a little faster than the binder, or that a molten layer exists on the burning propellant surface. Nevertheless, some general agreement has been reached on what occurs. Three separate cross sections perpendicular to the burning propellant surface are shown in figures 6, 7, and 8.

Figure 6 presents nomenclature, such as "fizz zone" and "foam zone," that has been observed to behave in the terms described(4). A mechanistic cross section is shown in figure 7. This model by Cantrell et al. (6) also includes combustion instability effects. A more physical interpretation (7) of the burning surface of a solid propellant is shown in figure 8.

As reported by Vantock(8), the Soviets also differentiate stages in the solid propellant combustion process. These stages are: (a) preheating of the propellant; (b) solid phase reactions; (c) melting; (d) liquid phase reactions; (e) evaporation; (f) sublimation or dispersion; and (g) homogeneous or heterogeneous reaction in the gas phase. Regardless of which model (whether figure 6, 7, or 8) is chosen it should be obvious that a complex process occurs across the interface between hot combustion gases and the unreacted solid propellant. For the time being it must be assumed that a real Lewis number, or an "effective" Lewis number, can be defined for the over-all combustion region.

It is significant to note that, rather than acknowledge the existence of such a complex function as a so-called "effective" Lewis number, the normal practice is to assume Le = 1.0. However, there have been evaluations of situations when Le ≠ 1.0. One of the best of these analyses is Lees(9). In boundary type flow systems with chemical reactions, heat energy is transported by heat conduction and the diffusion of species carrying chemical enthalpy. A heat flux vector, $\vec{q}$, can be defined to represent this over-all heat transport,

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Thus,

$$\dot{q} = - \frac{k}{c_p}\left[\left(\frac{\partial h}{\partial y} - \Sigma h_i \frac{\partial K_i}{\partial y}\right) + \frac{\rho D_{12}\bar{c}_p}{k}\Sigma h_i \frac{\partial K_i}{\partial y}\right] \quad (10)$$

$$\text{CONDUCTION} \qquad \text{DIFFUSION}$$

where: $h_i = \int_0^T c_{p_i} dT + h_i^\circ$

h_i° = heat of formation of i'th species

h = complete static enthalpy

$= \Sigma K_i h_i$

K_i = mass fraction of i'th species

D_{12} = binary mass diffusivity

$\bar{c}_p = \Sigma h_i c_{p_i}$

T = temperature

When the Lewis number equals unity in equation 10, the heat flux vector becomes

$$\dot{q} = - \frac{k}{\bar{c}_p}\frac{\partial h}{\partial y} \quad (11)$$

Equation 11 is similar to ordinary heat conduction for a non-reacting pure gas. This is usually a much easier equation to solve than equation 10. Even though the Lewis number may be eliminated from calculations by assuming it equal to unity, there is no overlooking the fact that the Lewis number has significance in physical phenomena. A qualitative interpretation of the Lewis number and equation 1 will indicate some of the phenomena involved in solid propellant combustion.

QUALITATIVE PREDICTION OF EXPONENT

Based upon equation 1, and experimental evidence, there are four major parameters that contribute to differences in solid propellant burning rates at constant pressure. These are:

a. Chemical Composition
b. Transport Processes
c. Chemical Kinetics
d. Physical Geometry

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Parameters a, b, and c can be partly related through use of figure 5. Assume a propellant is burning with the conditions and properties as shown in zone 1 of figure 5. If this hypothetical propellant is like a plateau or mesa propellant, its rate-pressure curve will change in the neighborhood of some pressure "x". What happens at x (which does not necessarily have to be a sharp transition) ? Supposedly, the kinetic order of the system changes between zones 1 and 2. In terms of the Lewis number the transition involves a coupling between transport properties and kinetic phenomena. In zone 1, it is hypothesized that reaction A → B predominates in the combustion process near the propellant surface. Under these conditions the Lewis number will remain constant and largely dependent upon the species B. As pressure increases to zone 2, then, reaction A → C becomes significant. A new species, C, now controls the flame properties and a new Lewis number is established. If the reaction does not change, the same Lewis number should predominate until increased pressure starts affecting the transport processes. Spectroscopic observations of the combustion zones of different types of propellants burning at different pressures could possibly prove or disprove this mechanism. Some data along this line have been reported by Tajima et al.(10). In these studies, spectroscopic data indicate that the same chemistry is taking place in the surface reaction zone of double-base propellants regardless of the pressure. No change in burning rate exponent was reported in these studies.

In considering figures 2 through 4, it should be obvious in the light of present experience, that certain propellant compositions have inherent burning characteristics. The problem, then, becomes one of how to modify these characteristics.

Combining equations 4 and 9 the following relationship of burning rate exponent and transport processes is obtained:

$$n = \phi\left(\frac{\text{Thermal diffusivity}}{\text{Mass diffusivity}}\right) \qquad (12)$$

Consequently the burning rate exponent will be increased by increases in the thermal diffusivity if the mass diffusivity remains unchanged. Increased mass transport will lower the exponent if no changes in thermal transport occur. However, it is difficult (if not impossible) to change the transport processes without changing the kinetic mechanism. It has been noted(4) that, at rocket pressures (below 2000 psi), n for the same propellant is generally lower than at gun pressures (10,000 to 50,000 psi). This is probably due to the fact that higher pressures tend to increase thermal diffusivity and retard mass diffusivity.

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As reported by Vantoch(10), it has been predicted and observed that combustion is stabilized with an increasing amount of heat released in the condensed phase. This would lead to a lowered thermal diffusivity and a correspondingly lower or more stable exponent. Vantoch(10) also reports that the effect of a catalyst in some cases is to cause a high surface temperature through heat release in the condensed phase. Heat transfer from the gas to the condensed phase would have to be small under these circumstances.

Another approach would be to cause an apparently artificial increase in the thermal diffusivity through external radiation or an additive that considerably increases the flame radiation. This could be done without appreciably disturbing the chemical steps in the reaction mechanism. A small amount of heavy metals might also disturb the mass diffusivity sufficiently to lower the exponent. Negative exponents are often observed when condensed residues from heavy metals or other additives are formed during combustion. When a condensed residue forms, the regression rate decreases with increasing pressure due to lowered heat transfer (10).

The orientation of metal fibers in a propellant could also cause increased thermal diffusivity, resulting in higher exponents. However, this effect also would depend upon the kinetics of the metal combustion process. If the metal fibers react at a rate less than the unmetallized propellant, the effect of the increased thermal diffusivity would be the same as a higher ambient temperature in the propellant. In this case, the over-all burning rate is increased with little or no change in burning rate exponent.

In equations 1 and 3, the quantity, "b", is the variable which depends primarily on the chemical kinetics. This conclusion is most readily apparent from the effect of initial temperature on propellant burning rates. Figure 9 illustrates this point (4). However, with equation 1 it becomes more evident that b is dependent on kinetics. The same effect as produced by variation in initial propellant temperature is also accomplished by the addition of catalysts to solid propellants. The exponent might be changed by adding a sufficiently large quantity of catalyst that the transport processes are affected. Catalysts which change the intermediate reaction steps might also cause a variation in exponent. After all, any change in composition or the geometry of constituents means a new propellant.

The effects of oxidizer particle size, propellant homogeniety, and physical geometry have been noted by Hall and Bastress(11). The results in general show the same variation as the effect of initial temperature or catalysts.

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Throughout this section, most of the comparison of propellant properties have been made at a constant pressure. However, pressure can be a significant variable, too. As mentioned before, the changes that occur in figure 5 at points x, y, and z are a function of pressure that are related to the intrinsic properties of the propellant. There is another significance to pressure that can best be identified by another hypothetical model propellant. These properties are shown in figure 10. Any of the typical propellant performance curves shown in figures 2, 3, and 4 could have been depicted in the "normal propellant operations" region of figure 10. The propellant, represented by figure 2, is a more common example. Pure ammonium perchlorate and most propellants made with this oxidizer show a nearly linear behavior over an extremely wide pressure range. In fact, rate-pressure measurements on a polybutadiene-acrylic acid composite propellant have been made by Cole(12) up to 60,000 psi in a self-pressurizing closed-bomb system. These studies did not exhibit a deflagration-to-detonation transition.

At very low pressures, the combustion zone broadens. Diffusion processes become controlling to the point where an extinction pressure is reached. Equation 1 conforms with such an approach.

Under certain conditions when confined in a bomb or subjected to an energy transferring impulse, the pressure rises at a very high rate. A transition then occurs from normal deflagration to a steady state detonation. If not suitably confined, the pressure rise may only result in a catastrophic explosion. Typical shock pressures for propellants may be 60 kilobars with "regression rates" of 5000 meters per second. However, before deflagration-to-detonation processes can be described in more detail, it is necessary to discuss the specific effect of variables on the burning rate exponent.

QUANTITATIVE PREDICTION OF EXPONENT

It would be desirable to be able to predict the magnitude of the burning rate exponent of a propellant from its physical properties. If this can not be done, it might also be just as desirable to predict the properties of one propellant from the properties of another. The following analysis considers the latter point.

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Using equation 1 and comparing propellant 1 against propellant 2,

$$r_1 = b_1 \, p_1^{\log(1/Le_1)} \tag{13}$$

$$r_2 = b_2 \, p_2^{\log(1/Le_2)} \tag{14}$$

For relative rates at equal pressures,

$$\frac{r_1}{r_2} = \frac{b_1}{b_2} \, p^{\log(1/Le_1) \, - \, \log(1/Le_2)} \tag{15}$$

$$\frac{r_1}{r_2} = \frac{b_1}{b_2} \, p^{\log(Le_2/Le_1)} \tag{16}$$

Make use of the following

$$a^x = e^{x \ln a} \tag{17}$$

$$a^{\ln b} = e^{\ln b (\ln a)} \tag{18}$$

This is the same as

$$b^{\ln a} = e^{(\ln a) \ln b} \tag{19}$$

Then,

$$a^{\ln b} = b^{\ln a} \tag{20}$$

or,

$$a^{\log b} = b^{\log a} \tag{21}$$

The identity above can be used in equation (16) so that:

$$\frac{r_1}{r_2} = \frac{b_1}{b_2}\left(\frac{Le_2}{Le_1}\right)^{\log p} \tag{22}$$

Since,

$$Le = \frac{\rho D c_p}{k} \tag{23}$$

$$\frac{r_1}{r_2} = \frac{b_1}{b_2}\left(\frac{\dfrac{\rho_2 D_2 c_{p_2}}{k_2}}{\dfrac{\rho_1 D_1 c_{p_1}}{k_1}}\right)^{\log p} \tag{24}$$

Assume

$$\rho_1 = \rho_2 \quad , \quad c_{p1} = c_{p2} \quad , \quad D_1 = D_2$$

$$\frac{r_1}{r_2} = \frac{b_1}{b_2}\left(\frac{k_1}{k_2}\right)^{\log p} \tag{25}$$

The results of the above analysis may be summarized. An increase in burning rate from r_1 to r_2 results if the following relative changes in variables occur:

$r_2 > r_1$ if: $b_2 > b_1$, other variables equal

$k_2 > k_1$, other variables equal

$\rho_2 < \rho_1$, other variables equal

$D_2 < D_1$, other variables equal

$c_{p_2} < c_{p_1}$, other variables equal

$\alpha_2 > \alpha_1$, other variables equal

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Data from a study by Sabadell and Wenograd[13] were used to make calculations related to equations 22 to 25. In the studies by Sabadell and Wenograd the surface temperatures and thermal conductivities of a series of PBAA-ammonium perchlorate propellants were measured. The composition of the propellants of interest are shown in Table 2. Composition 70F was used as a base to calculate a Lewis number. The following values were calculated or assumed as order-of-magnitude quantities:

$$\rho \quad = \quad 1.8 \text{ grams/cm}^3$$

$$c_p \quad = \quad 1.0 \text{ cal/}^{\circ}\text{C}$$

$$\log(\frac{1}{Le}) \quad = \quad 0.255$$

$$k \quad = \quad 5.3 \times 10^{-4} \quad \text{cal/}^{\circ}\text{C-cm-sec}$$

$$p \quad = \quad 15 \text{ psig}$$

$$D \quad = \quad 1.652 \times 10^{-4} \text{ cm}^2\text{/sec}$$

Other measured values of thermal conductivity were substituted into $\log (1/Le)$ to determine the calculated exponents in Table 3.

The calculated burning rate exponents do not agree too closely with the measured values. However, the calculated quantities bracket the measured exponent for the two different thermal conductivities used. It is significant to note how the changes in thermal conductivity change the calculated exponents. Some other properties such as density or diffusivity must also have changed with the thermal conductivity. Otherwise, the exponent of the individual PBAA propellants would not remain constant over a pressure range. In any case, no other example was discovered in this review where burning rate exponents of one propellant were predicted from properties of another propellant formulation. This example provides a crude but quantitative demonstration of equation 1.

DEFLAGRATION -TO-DETONATION

There are circumstances under which a burning, or deflagrating propellant begins to regress at a higher and higher rate. Zone 4 in figure 5 represents this condition. Predictions of the mechanisms of deflagration-to-detonation (abbreviated as DTD) can be made with the aid of equation 1. In order to do this it is necessary

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first to refer to figure 11. The pressure versus inverse density relationship shown in figure 11 is known as a Hugoniot plot. Two regions exist in this plot with a discontinuity between the two curves. As noted, one curve describes conditions for detonation and the other designates deflagration.

In order to correctly predict the influence of the Lewis number on DTD, it is necessary to refer to both figure 5 and figure 11. Consider the deflagration curve in figure 11. As the density gets smaller, the deflagration curve approaches the abscissa. Apparently, the density could decrease to zero and the deflagration curve could be extended asymtotically. However, according to equations 1 and 4, as the density approaches zero, the burning rate exponent approaches an infinite magnitude. This is contrary to figure 5 as well as experience. The burning rate exponent must remain less than unity if deflagration is to be sustained. A value of n greater than unity would lead to a detonation. The transition of n to greater than unity occurs in equation 4 for a Lewis number of about 0.1. Thus, in figure 11 a critical density is predicted where the deflagration curve involves a transition to detonation. Observations of this effect have been recorded by Gordon(15). It has also been observed that decreasing the bulk density of a propellant, such as shredding it, will cause an otherwise non-sensitive material to detonate. If the Lewis number is slightly less than unity, a small decrease in density could cause the Lewis number to exceed unity. This would cause n as defined by equation 4 to yield a runaway reaction. It is also possible that the same process of shredding, or high porosity, could lead to higher localized thermal diffusivity, such as a hot spot (16). According to equation 9, this would also lead to a transition to detonation. Thus, both the effects of porosity and the potential existence of hot spots are predicted by equation 1.

In equation 1, when the Lewis number is unity, the regression rate is apparently not a function of pressure. The value of r is dependent on the kinetic function b only. Consequently, in figure 11, the discontinuity between the detonation and deflagration curves probably occurs for Le = 1.0.

The various values of Lewis number and burning rate exponent that exist for figure 11 are tabulated in Table 4. Zone 3 in figure 5 is also indicated under the deflagration curve. This is an unusual case where diffusion-related phenomena predominate. The case when Le = 1.0 is explained by the following postulation. Assume that transport processes and chemical kinetics can be competing mechanisms, even in a detonation. In addition, there is always a coupling between these mechanisms. When a shock is passed through an explosive, the

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shock effects both the transport processes and kinetics. Suppose that the Lewis number is unity, and is unchanged by a shock. The processes contributing to reaction kinetics are then controlling when a shock passes through the propellant. The shock must be equal to or greater than the energy barrier required to initiate the detonation. If the shock is not intensive enough, there will be no detonation because the Lewis number is unity. With a sufficiently intensive shock, a steady state detonation is established. This is the general mechanism of a high order detonation. The detonation model supported by Eyring and coworkers, as quoted by Boyer(17), follows this latter model. According to these investigators the high regression rates of a detonating grain in the grain burning process effectively prevents conduction of heat into the unburned solid.

A true deflagration-to-detonation event requires the Lewis number properties given in Table 4. There are also circumstances where an explosive receives a shock that is insufficient for a high order detonation. However, the shock influences the Lewis number such that it exceeds unity. The reaction grows at a rapid pace because of the high pressure inherent in the initial shock. Rapidly the explosive reaches a steady-state detonation. But, this process requires several more microseconds than a high order detonation. This slower process where transport processes are significant results in the so-called low order detonation phenomena.

The Lewis number can be unity for either a detonating or deflagrating system. As noted above, if Le = 1.0, a sufficient shock must be used to achieve a detonation. After a steady-state detonation is achieved, the Lewis number always adjusts to unity. Otherwise, the reaction rate would increase indefinitely. It might be hypothesized that the mechanisms for all transport-related phenomena become equivalent in detonation or supersonic flow systems. For a deflagration, the Lewis number can be any value above about 0.1.

Some justification for the above mechanism may be provided by combustion instability studies. As noted by Vantoch(10), combustion instability may precede deflagration-to-detonation transition. A pulse created through combustion instability may be caused to grow. According to Zucrow(18), any effect which contributes to an increase in static temperature of an element of gas, such as chemical heat addition, will help to amplify a pulse. This could also cause an increase in thermal diffusivity sufficient for a detonation to occur.

Although not defined in this paper, the existence of a critical diameter for propellants and explosives is also probably a function of the Lewis number and transport processes.

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CONCLUSIONS

It has been postulated by the author that the burning rate exponent for solid propellant combustion can be represented by

$$n = \log (1/\text{Lewis number})$$

The Lewis number, Le, is the ratio of mass diffusivity to thermal diffusivity. Although this new burning rate exponent function of Le has not been rigorously derived, evidence has been collected to justify some aspects of its validity. Such a function must have more than just a fortuitous significance in view of the following:

1. Measured values of "n" substituted in the correlation produce reasonable order-of-magnitude numerical values for Le.

2. The Le function offers a single parameter as a unified explanation for normal, mesa, plateau and negative burning, and deflagration-to-detonation behavior of solid propellants. This is the first correlation to cover such a broad regime.

3. In comparing the burning rate properties of two different propellants, the Le correlation predicts the observed relationships of density, specific heat, and thermal conductivity.

4. Calculations on a selected propellant system gave an order of magnitude prediction of the burning rate exponents of two propellants as related to a third propellant.

5. The Le correlation complies with observed qualitative effects of variations in heat and mass transport.

6. The Le correlation predicts a critical density effect in detonation phenomena.

7. The burning rates of solid propellants are expressed in the Le correlation as a function of heat transfer divided by mass transfer. It does not make any difference whether the numerator approaches infinity or the denominator becomes negligibly small, the burning rate increases very sharply. This essentially shows that deflagration-to-detonation analyses can use either mass-diffusivity or heat-resistance controlled grain burning models.

8. A coupling effect between transport properties and kinetic phenomena is exhibited by the Le correlation. As long as the reaction A $\longrightarrow$ B predominates, the value of Le will remain constant and dependent upon the species "B". As pressure increases, then, the reaction A $\longrightarrow$ C may become important. In this case, a new Le is

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determined by the species "C". Such a pressure effect on the controlling reaction in solid propellant combustion has been observed.

9. The Le correlation allows a very wide pressure dependency which has been a weakness in other burning rate models.

Even though all of the above may be true, it is still necessary to observe that the "effective Le" involved in solid propellant combustion may be extremely difficult or impossible to define. Nevertheless, the Le correlation defined may be an effective tool for analyzing the proper relationships of variables in solid propellant combustion, or heterogeneous reactions in general.

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REFERENCES

1. Heaston, R. J., Private communication to Dr. Leon Green, Lockheed Propulsion Company, Redlands, California (15 March 1963)

2. Heaston, R. J., Private communication to Mr. Douglas Ordahl, United Technology Center, Sunnyvale, California (15 March 1963)

3. Heaston, R. J., "Solid Propellant Combustion Research (U)", Proceedings of Interagency Solid Propulsion Meeting, Seattle, Washington, CONFIDENTIAL (1963)

4. Ball, A. M., "Solid Propellants - Part I", Ordnance Engineering Design Handbook - Explosives Series, ORDP 20-175

5. Foust, A. S. et al., "Principles of Unit Operations", John Wiley & Sons, Inc., New York (1960)

6. Cantrell, R. H., McClure, F. T., and Hart, R. W., "Effects of Thermal Radiation on the Acoustic Response of Solid Propellants", Report TG 335-18, Applied Physics Lab., The Johns Hopkins Univ., Silver Springs, Maryland, p. 8 (June 1964)

7. Murthy, S. N. B., Hoffman, J. D., and Lehmann, G. M., "Interaction of Pressure Disturbances with Combustion Regions in Rocket Motors", Proceedings of the 1st ICRPG Combustion Instability Conference, CPIA Publication No. 68, pp 73-92 (January 1965)

8. Vantoch, P., "Combustion Instability in Solid-Propellant Rockets", Foreign Science Bulletin, Vol. 1, No. 9, Aerospace Tech. Div. Library of Congress, pp 1-29 (September 1965)

9. Lees, Lester, "Convective Heat Transfer with Mass Addition and Chemical Reactions", Combustion and Propulsion, Third AGARD Symposium, p. 451-498 (1958)

10. Tajima, Y. A. et. al., "A New Experimental Technique and New Results on the Mechanism of Combustion and Catalysis of Double Base Propellants", Abstracts of the 2nd Combustion Conference, CPIA Publication No. 95, p. 61 (September 1965)

11. Hall, K. P. and Bastress, E. K., "Burning Rate Control Factors in Solid Propellants", Princeton University, Sixth Quarterly Technical Summary Report, Contract NOW 1858 (32) - NR 098-201 (15 July 1960)

12. Cole, R. B., "High Pressure Solid Propellant Combustion Studies using a Closed Bomb", Rohm & Haas Co. Special Report No. S-68, Huntsville, Alabama (1965)

13. Sabadell, A. J. and Wenograd, J., "The Measurement of the Temperature Profiles of Burning Solid Propellants by Micro-thermocouples", Princeton University, Aeronautical Engineering Report No. 664 (September 1963)

14. Wolfson, B. T., "The Effect of Additives on the Mechanism of Detonation in Gaseous Systems", PhD Dissertation, Ohio State University, Columbus, Ohio, p. 376 (August 1963)

15. Gordon, W. E., "Detonation Limits in Condensed Explosives", Preprints of the Fourth Symposium on Detonation, Vol. 1, Office of Naval Research, p. A163 (October 1965)

16. Macek, Andrej, "Sensitivity of Explosives", Chemical Reviews, 62, 41 (1962)

17. Boyer, M. H., "Study of Detonation Behavior of Solid Propellants", 16th Quarterly Report, Contract NOrd 17945, Task 1, Aeronutronic Res. Lab., Newport Beach, California (November 1961)

18. Zucrow, M. J. et. al., "Parametric Study on Rocket Motor Instability", Abstracts of the 2nd Combustion Conference, CPIA Publication No. 95, p. 26 (September 1965)

TABLE 1

RELATIONSHIP OF LEWIS NUMBER

TO BURNING RATE EXPONENT

Measured Exponent	Rate-Pressure Curves	Calculated Lewis No.	Description of Gas
0.1 - 0.7	Normal or Progressive	0.8 - 0.2	Real
0	Plateau or Mesa	1.0	Ideal
< 0	Negative or Regressive	> 1	Complex
→ ∞	Deflagration to Detonation	→ 0	Dense

TABLE 2

PROPELLANT COMPOSITIONS

Propellant Designation	Components - Percent in Weight					
	PBAA	EPON 828	AP Fine 9 Micron	AP Coarse Ground	Copper Chromite	Ferric Oxide
70F	25.7	4.3	70	---	---	---
70F-1C	25.7	4.3	70	---	1	---
70F-1FO	25.7	4.3	70	---	---	1
75 BM	21.4	3.6	22.5	52.5	---	---

TABLE 3

COMPARISON OF MEASURED AND CALCULATED BURNING RATE EXPONENTS

Propellant Designation	Pressure psig	Thermal Conductivity cal/°C-cm-sec	Measured n	Calculated n
70F	15	5.3×10^{-4}	0.255	Base
	100	8.4×10^{-4}	0.255	Base
70F-1C	15	10.9×10^{-4}	0.381	0.563
	100	18.6×10^{-4}	0.381	0.364
70F-1FO	15	10.6×10^{-4}	0.410	0.551
	100	15.3×10^{-4}	0.410	0.352
75 BM	15	5.5×10^{-4}	0.291	0.266

TABLE 4

EFFECT OF VARIABLES IN LEWIS NUMBER ON DEFLAGRATION TO DETONATION

Variable	Detonation	Uncertain	Deflagration
Le	0 to 0.1	1.0	0.1 to <1; >1.0
n	>1.0	0	>0 to <1; <0
ρ	Low	---	High
D	Low	---	High
c_p	Low	---	High
k	High	---	Low
α	High	---	Low

$$r = bp^{\log\left(\frac{1}{Le}\right)}$$
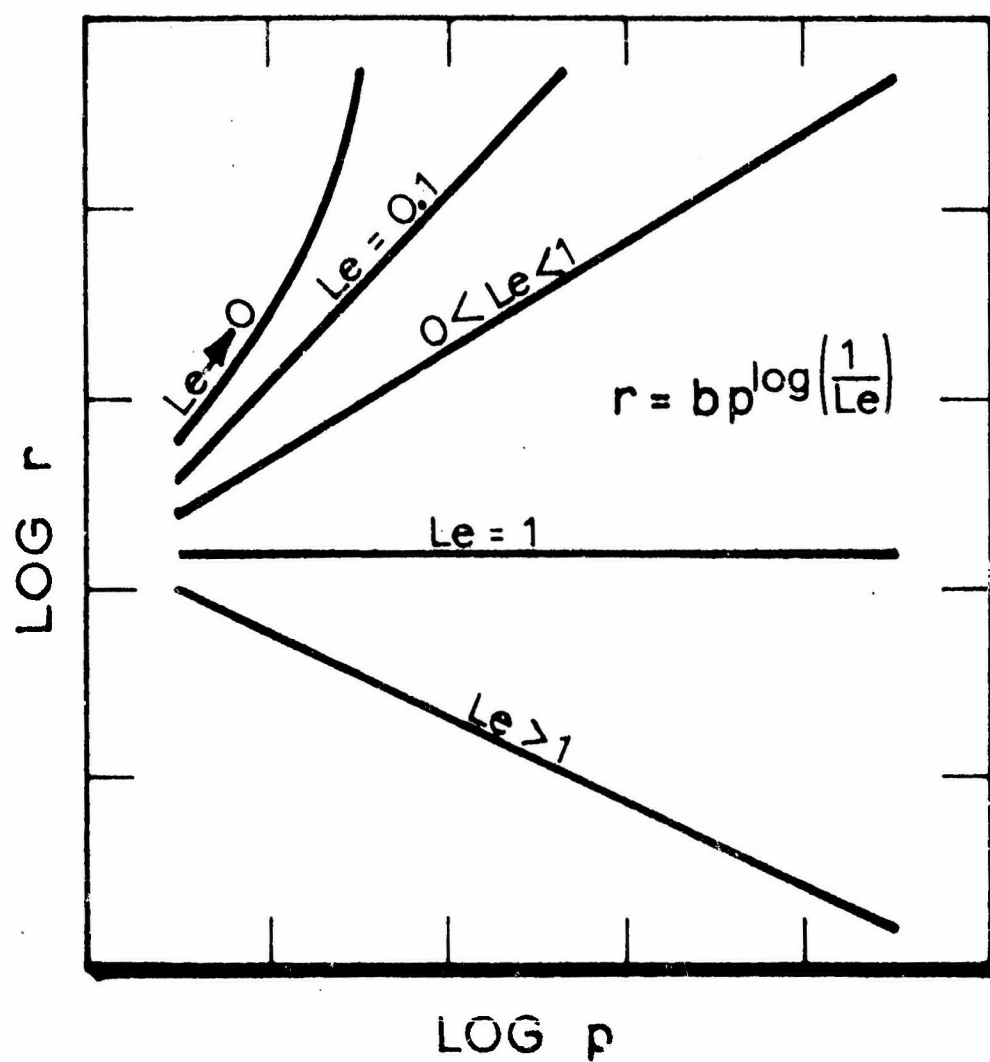
Fig. 1   Effect of Lewis Number on r-p Relationships
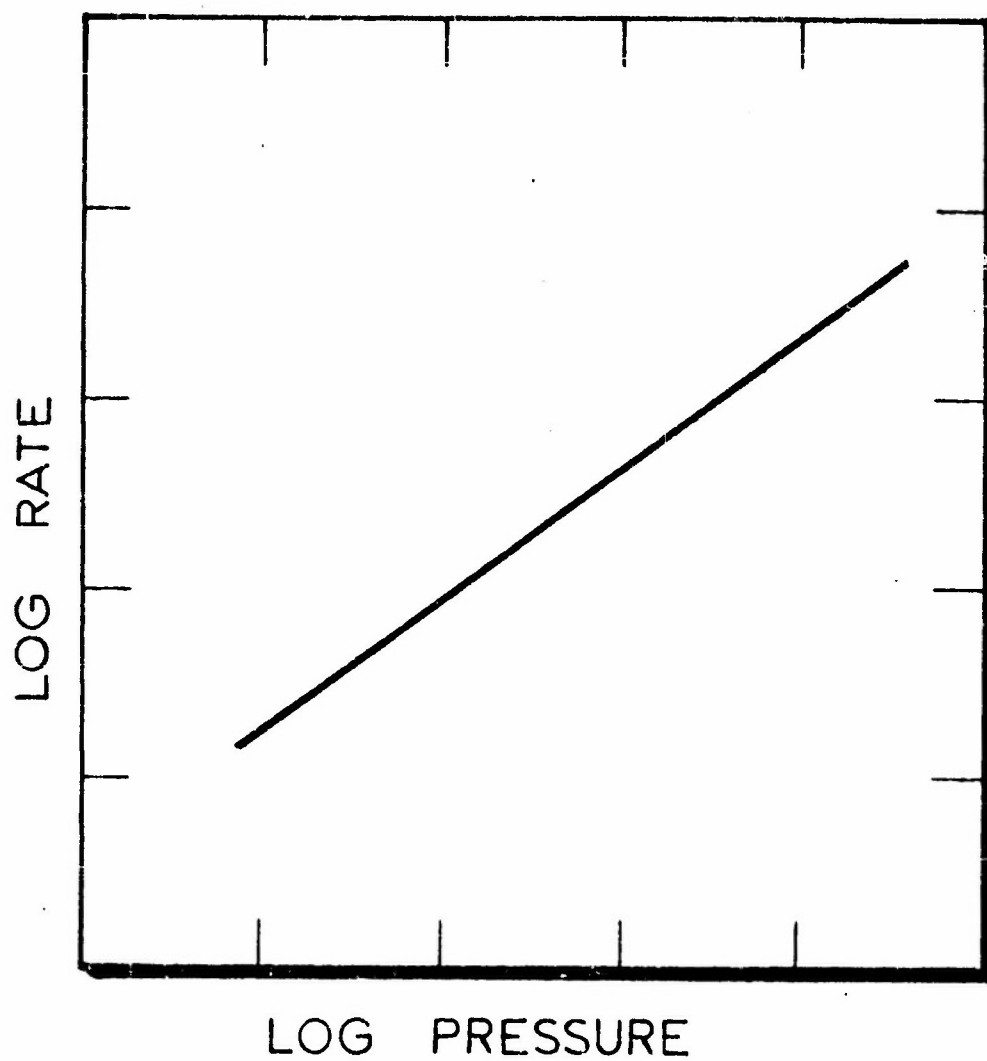
Fig. 2   Normal Rate-Pressure Relationship of Propellants
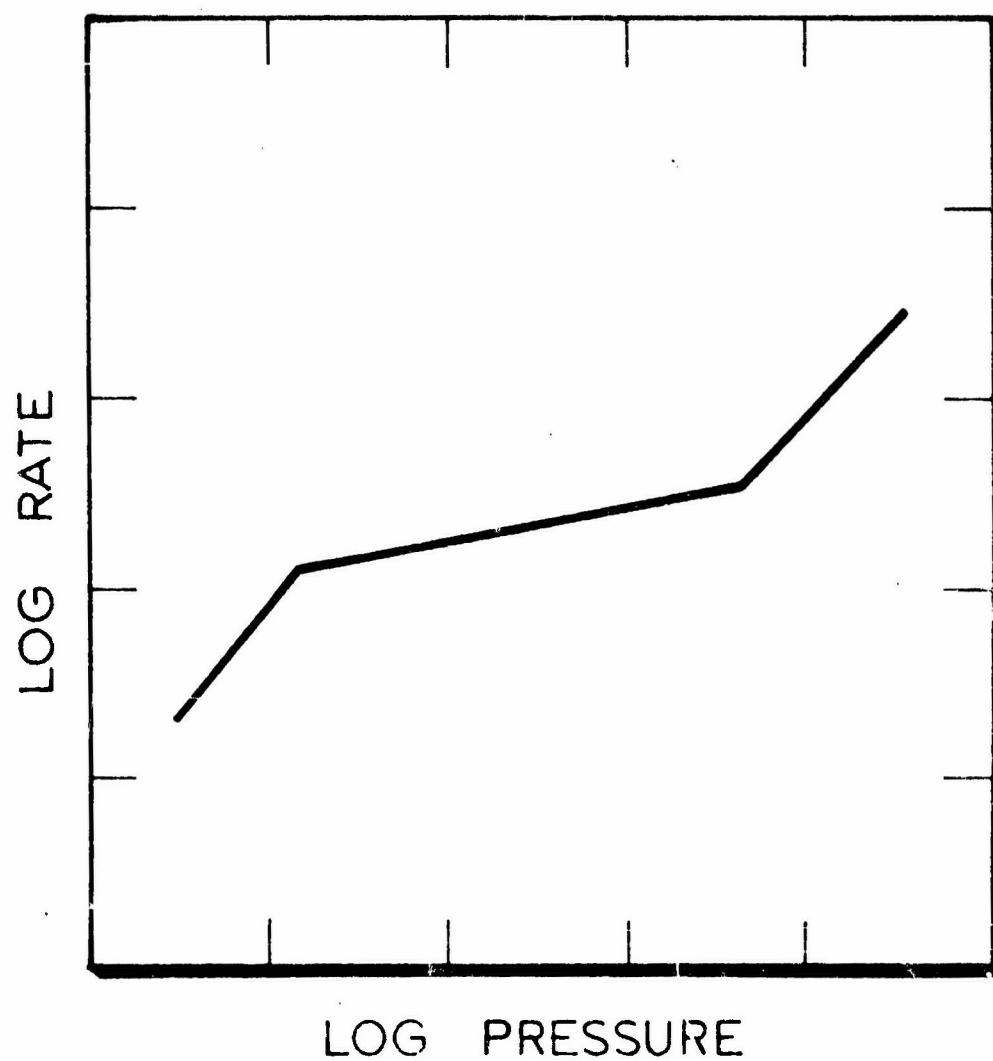
Fig. 3   Rate-Pressure Relationship of Plateau Propellants

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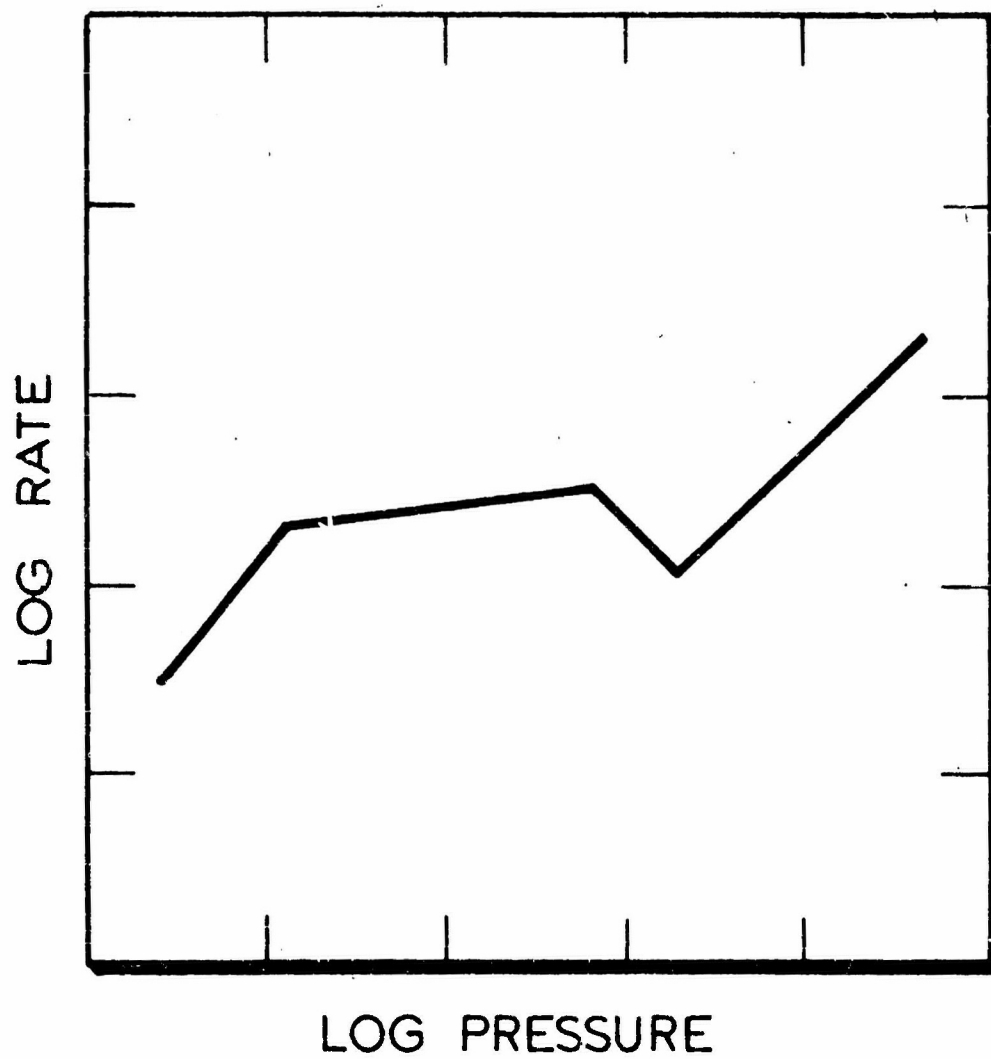
Fig. 4   Rate-Pressure Relationship of Mesa Propellants
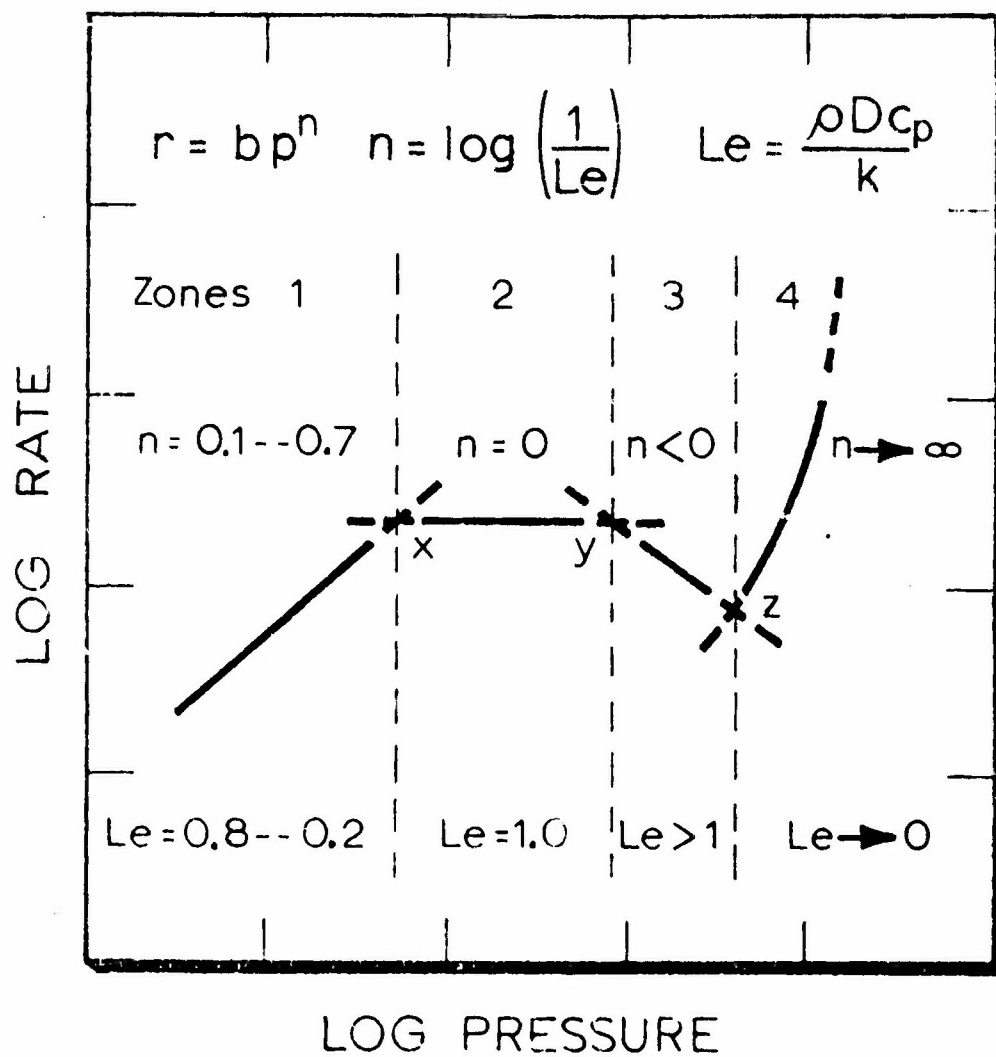
Fig. 5   Hypothetical Rate-Pressure Diagram to Show
Different Propellant Characteristics

|←—0.01 inches Total Depth —→|
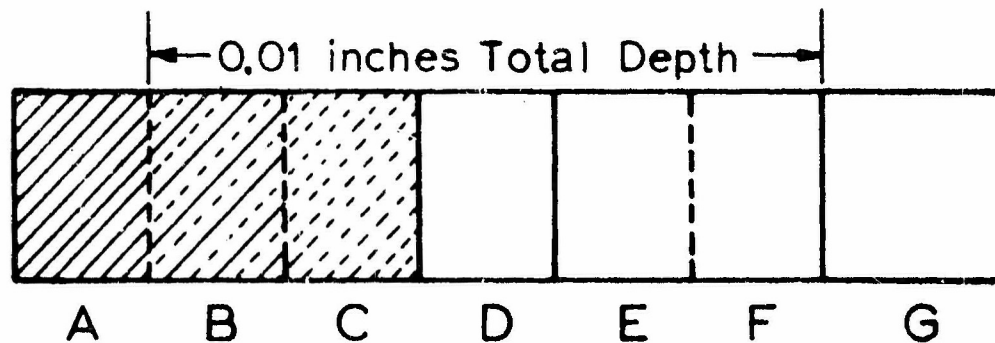
A COLD PROPELLANT

B HEATED PROPELLANT

C PYROLYSIS ZONE (FOAM ZONE)

D PRIMARY GASEOUS PYROLYTIC
   PRODUCTS

E GAS HEATING ZONE (FIZZ ZONE)

F GAS REACTION ZONE (FLAME ZONE)

G BURNED GAS

Fig. 6   Burning of a Solid Monopropellant
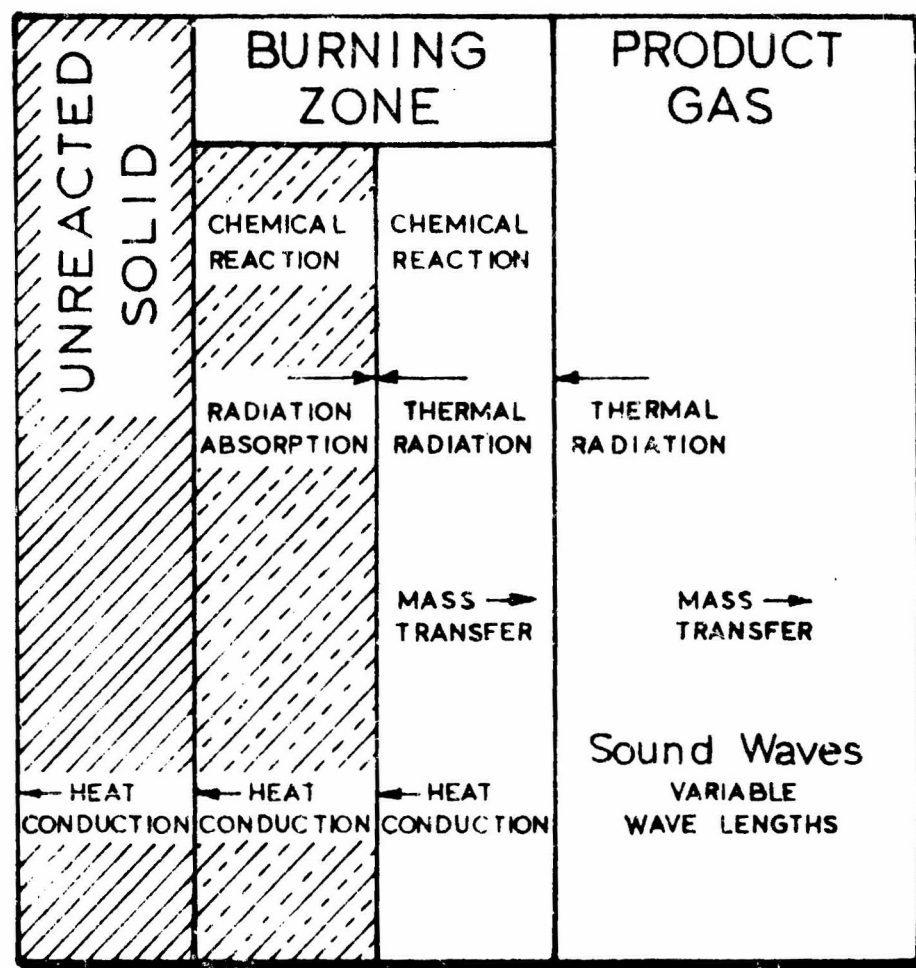
Fig. 7   Structure of Boundary Region Associated with a
         Burning Propellant

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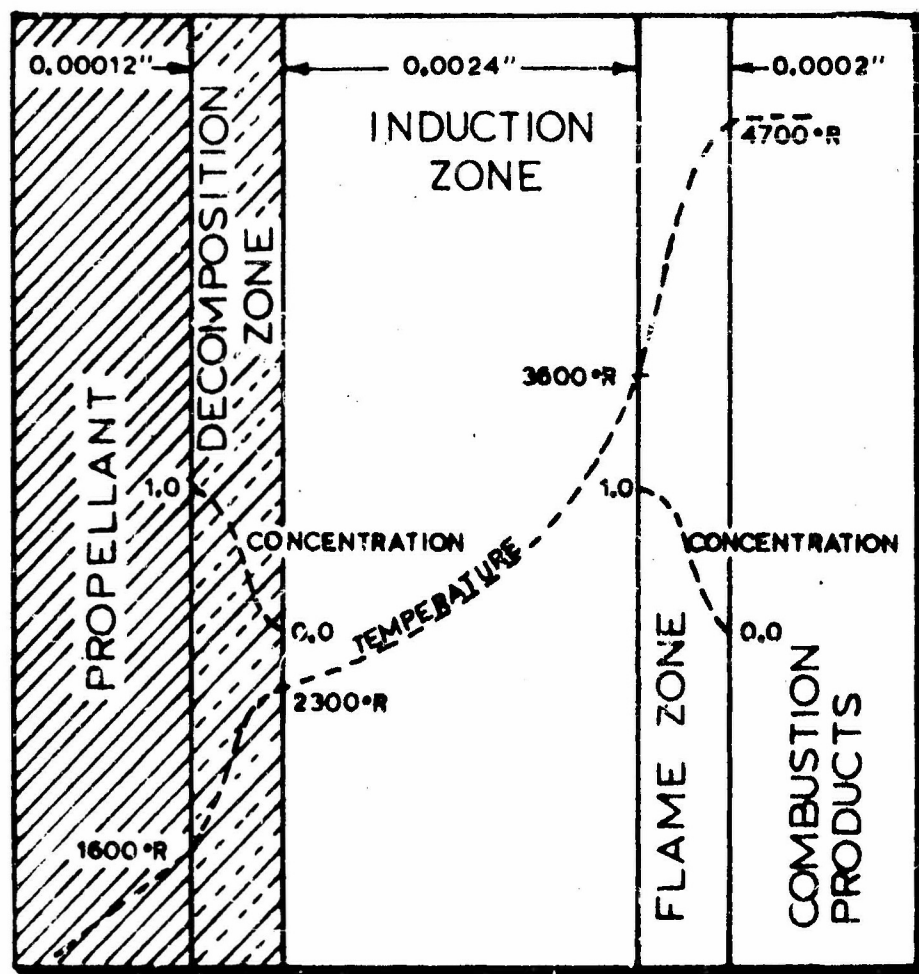
Fig. 8   The Combustion Region Adjacent to the Burning
          Surface of a Solid Propellant (80% AP – 20% PBAA)
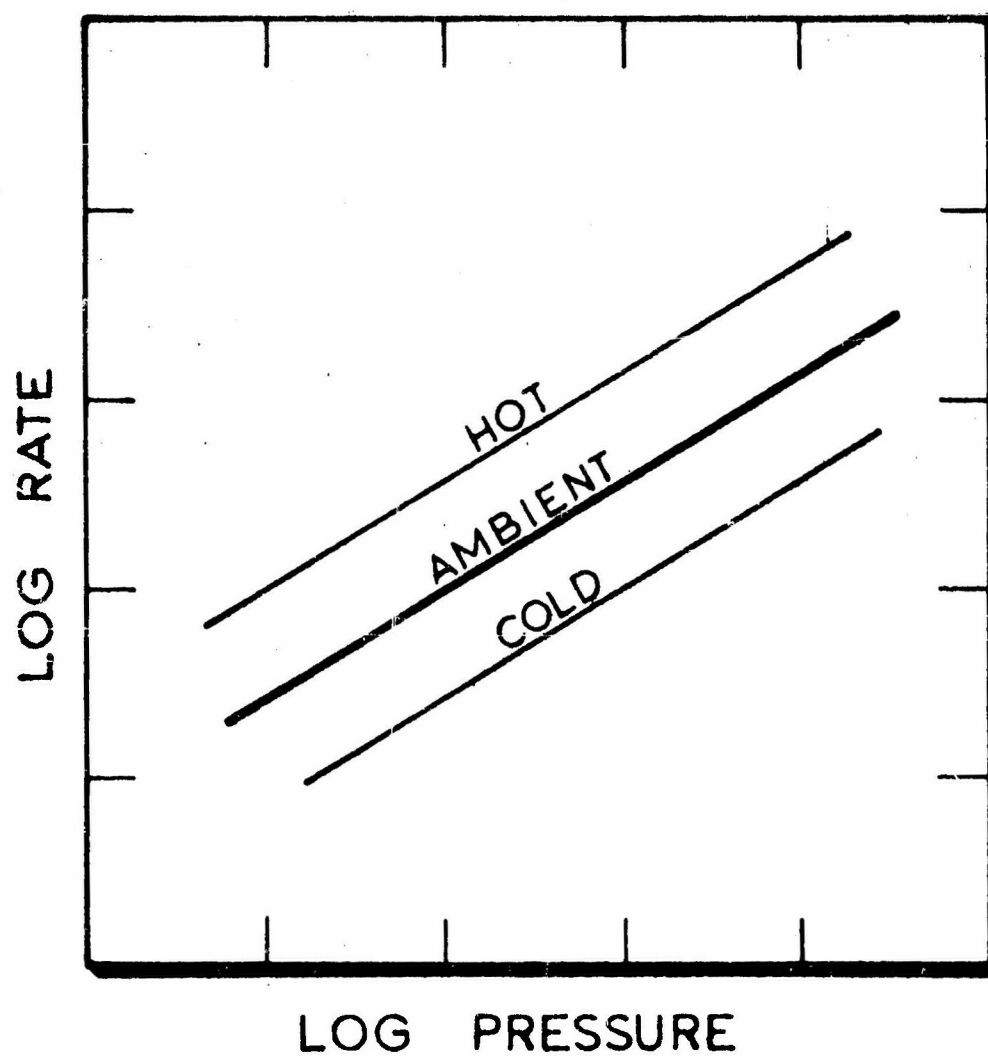
Fig. 9 Effect of Initial Temperature on Rate-Pressure Relationship
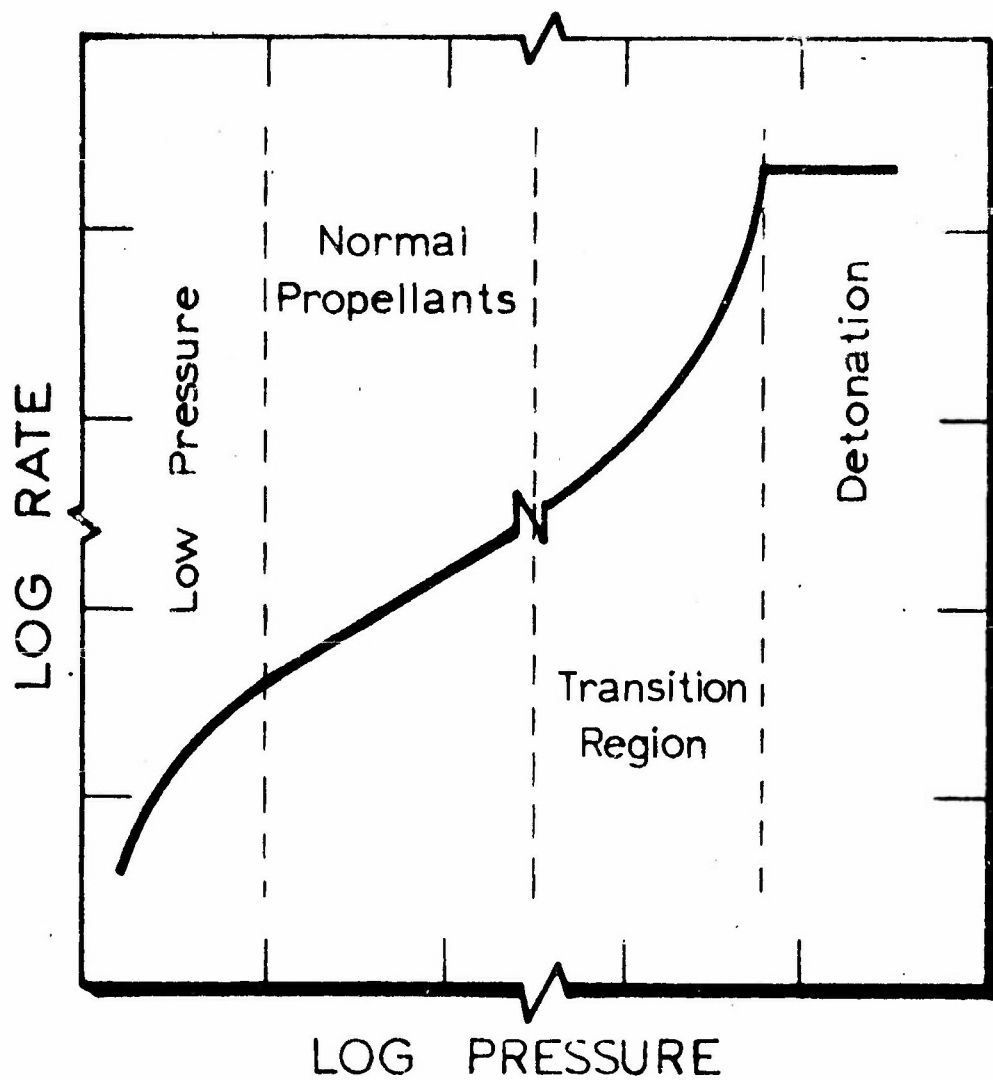
Fig. 10   Variation of Burning Rate over a Wide Pressure Range
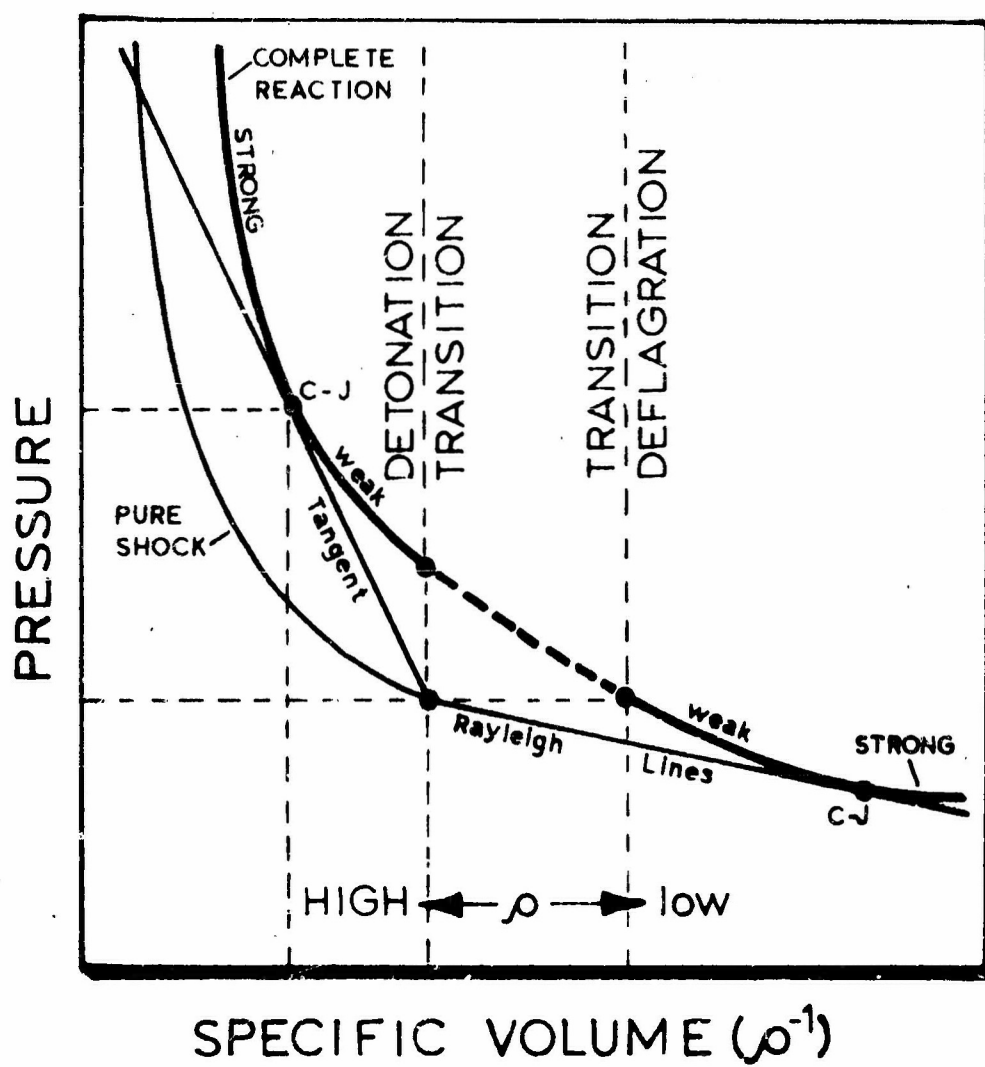
Fig. 11   Hugoniot Diagram

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13. ABSTRACT

It has been postulated by the author that the burning rate exponent for solid propellant combustion can be represented by

$$n = \log \ (1/\text{Lewis number})$$

The Lewis number, Le, is a dimensionless ratio of mass diffusivity to thermal diffusivity. The Lewis number correlation is used in the paper to explain burning rate versus pressure behavior for various progressive, plateau, and regressive propellants. Qualitative prediction by the correlation of observed relationships of heat and mass transport, density, specific heat, and thermal conductivity is described. Discussion is also presented on use of the model to predict a critical density effect in deflagration-to-detonation phenomena.

Using a selected PBAA-ammonium perchlorate propellant as a base, the burning rate exponents of two other similar propellants were calculated. Calculated exponent values, using the Lewis number correlation, were within 10 to 25 percent of measured exponents.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Deflagration-to-detonation of solid propellants						

SUPPLEMENTARY

INFORMATION

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